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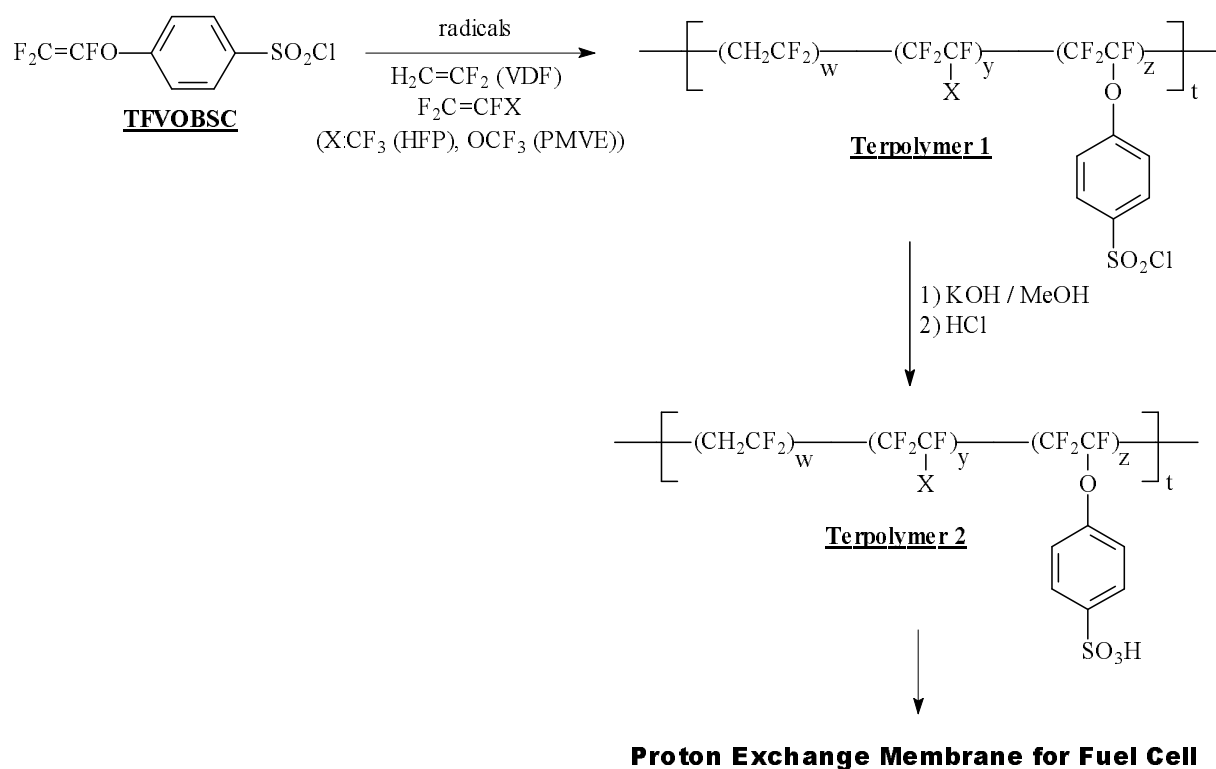
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GRAPHICAL ABSTRACT



**Proton-conducting polymer electrolyte membranes based on fluoropolymers
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Synthesis and characterizations**

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ABSTRACT: This paper presents the synthesis of new polymer electrolyte membranes based on fluoropolymers incorporating aromatic perfluorovinyl ether sulfonic acids. A novel synthetic route describing the preparation of perfluorovinyl ether monomer containing sulfonic functionalities, 4-[(α,β,β -trifluorovinyl)oxy]benzene sulfonic acid (TFVOBSA), is reported. The radical (co) and terpolymerization of 4-[(α,β,β -trifluorovinyl)oxy]benzene sulfonyl chloride (TFVOBSC) with 1,1-difluoroethylene (or vinylidene fluoride, VDF), hexafluoropropene (HFP), and perfluoromethyl vinyl ether (PMVE) is described. The terpolymers of TFVOBSC with VDF and HFP, or VDF and PMVE, were hydrolyzed and led also to original fluorinated terpolymers bearing sulfonic acid aromatic side-group. The terpolymers were characterized by ^1H and ^{19}F NMR spectroscopies, SEC, DSC and TGA. Membranes incorporating these functional fluoropolymers were prepared and the electrochemical (IEC, proton conductivity, swelling rates) properties were studied and discussed.

Keywords: Proton Exchange Membranes for Fuel Cell, [(α,β,β -trifluorovinyl)oxy] benzene sulfonic acid, vinylidene fluoride (VDF), hexafluoropropene (HFP), perfluoromethyl vinyl ether (PMVE), radical copolymerization, fluoro-membranes, electrochemical properties.

Introduction

Polymeric materials functionalized by acid groups have dominated as the ion-exchange component for application as membranes in proton exchange membrane for fuel cells (PEMFC)¹. Polymers for PEMFC are divided in two categories.

The first one, encompassed non-fluorinated polymers (Table 1) like sulfonated polystyrenes (crosslinked or not)², sulfonated polyimides (PI)³, sulfonated poly(aryl ether sulfones)⁴, sulfonated poly(aryl ether ketones)⁵, sulfonated phenol formol resins⁶, sulfonated poly(phenylene oxide)⁷, phosphonic poly(phenylene oxide)⁸, sulfonated silicates⁹, sulfonated poly(benzimidazole)⁹ and sulfonated organic-inorganic hybrids¹⁰.

Insert Table 1

On the other hand, fluorinated polymers are very interesting materials because of their outstanding properties¹¹, and are currently used as materials for the preparation of ion exchange resins^{12,13}, proton exchange membrane for fuel cell (PEMFC)¹⁴⁻¹⁵ and are commercially available under the names of Nafion[®], Flemion[®], Hyflon[®] or Aciplex[®] trade names^{16,17}.

Fluoropolymers for fuel cell can be divided in two groups (Table 2). First, are the polymers incorporating aliphatic monomers. These monomers can be functionalized by a sulfonic acid or a sulfonyl fluoride function (the corresponding sulfonic acid component was obtained by hydrolysis) like trifluorovinyl sulfonyl fluoride¹⁸⁻²⁰ or perfluorosulfonyl fluoride ethoxy propyl vinyl ether, monomer produced by Nafion[®]: $(F_2C=CF-(OCF_2CF(CF_3))_p-OCF_2CF_2SO_2F)^{21}$, $(F_2C=CF-OCF_2CF_2SO_2F)^{1b,22,23}$, or $F_2C=CF_2OCF_2OC_2F_4SO_2F^{24,25}$, or $F_2C=CF_2OCF_2CF(CF_3)OC_2F_4R$, $F_2C=CF-OCF_2CF(CF_3)OCF_2CF_2G$ (G: $SO_2NHSO_2CF_3$, $N(Na)SO_2CF_3$ or $N(Na)SO_2C_4F_8SO_2N(Na)SO_2CF_3^{26}$). The comonomer is usually tetrafluoroethylene (TFE) but can be also vinylidene fluoride (VDF or VF_2) with perfluorovinyl ethoxy sulfonyl fluoride²⁷, perfluorosulfonyl fluoride ethoxy propyl vinyl ether (PSEPVE)^{28-29a,29b}, functional comonomers as $F_2C=CF_2OCF_2CF(CF_3)OC_2F_4R^{30,31}$ where R stands for $NHSO_2CF_3^{26,32}$, $SO_2CLi(SO_2CF_3)_2$, $SO_2NLiSO_2CF_3$ and SO_2F (PSEPVE)³¹. These monomers can also be functionalized by carboxylic acid group^{27,28,30}, $H_2C=CF_2OCF_2CF(CF_3)CF_2CO_2CH_3^{29c}$, $F_2C=CF_2OCF_2CF(CF_3)OCF_2CF_2COOCH_3^{31}$, $F_2C=CF_2OCF_2CF_2COOCH_3^{32}$. Finally, they can be functionalized by phosphonic acid

groups^{8,33,34} like diethyl perfluoro(3-vinyloxypropyl) phosphonate²⁷, $\text{F}_2\text{C}=\text{CFP}(\text{O})(\text{OH})_2$ ³⁵. Furthermore, various functional trifluorovinyl monomers have also been prepared, bearing either a carboxylic acid³⁶, or a sultone³⁷.

The second group of fluorinated membranes are those which are prepared from (co)polymers incorporating an aromatic fluoromonomer³⁸ (Table 2). As a matter of fact, during the last decades, fluoropolymers incorporating aromatic monomers with sulfonic acid like perfluorovinyl aryl ether¹³, trifluorostyrene^{15a,39}, or with a phosphonic acid^{15b,40,41}, have found a growing interest. In the case of trifluorostyrene (functionalized by a phosphonic acid, or by halogenosulfonyl group post hydrolyzable into sulfonic acid), polymer prepared from them are obtained by their (co)polymerization with trifluorostyrene (TFS). Concerning, the perfluorovinyl aryl ether, the materials are synthesized by thermocyclodimerization $[2\pi+2\pi]$ ^{21,23a,23b,42,43} giving thermoplastic and thermoset polymers containing perfluorocyclobutane rings (PFCB). Such thermocyclopolymerization is usually observed at temperature ranging between 150 and 210 °C^{42,43}.

Insert Table 2

To the best of our knowledge, it can be observed that before 2004, no fluorinated membrane for PEMFC prepared from a (co) or a (ter)polymer obtained by radical (ter)polymerization, of $[(\alpha,\beta,\beta\text{-trifluorovinyl)oxy}]$ benzene halogenosulfonyl with fluoroalkenes has already been achieved. Hence, the objective of this paper concerns the synthesis and the characterization of a new generation of original membranes prepared from aromatic fluorinated copolymers^{38,40} incorporating fluoroalkenes such as VDF, hexafluoropropene (HFP, $\text{F}_2\text{C}=\text{CFCF}_3$), perfluoromethylvinylether (PMVE, $\text{F}_2\text{C}=\text{CFOCF}_3$) and an aromatic fluorinated monomer functionalized by a sulfonic acid. First, the syntheses and the (ter)polymerizations of $[(\alpha,\beta,\beta\text{-trifluorovinyl)oxy}]$ benzene halogenosulfonyl are presented. The second part concerns the preparation of proton exchange membranes for fuel cell. Finally, the physico-chemical and electrochemical characterizations of the materials were investigated.

Experimental Part

Materials

Vinylidene fluoride (VDF), hexafluoropropene (HFP) and 1,1,1,3,3-pentafluorobutane were kindly offered by Solvay Solexis S.A., Tavaux, France and Brussels, Belgium. Perfluoromethylvinyl ether (PMVE, Fluorochem), 1,2-dibromotetrafluoroethane, and 2,5-Bis(*tert*-butylperoxy)-2,5-dimethylhexane, tech, 90% (Luperox 101[®]) (Aldrich Chimie, 38299 Saint Quentin-Fallavier, France) were used as supplied. *t*-Butyl lithium (1.7 M in hexane) and Sulfonyl dichloride were used as received. Acetonitrile, Dimethylsulfoxyde, N-methyl pyrrolidinone of analytical grade, diethyl ether (Aldrich Chimie, 38299 Saint Quentin-Fallavier, France), were distilled over calcium hydride prior to use.

Analysis

The compositions of the terpolymer (the molar contents of VDF, PMVE or HFP and TFVOBSA monomeric units in the prepared terpolymer), were determined by ¹⁹F NMR spectroscopy. The NMR spectra were recorded on Bruker AC 200 and AC 250 instruments, using deuterated acetone as the solvent and TMS (or CFC1₃) as the references for ¹H (or ¹⁹F) nuclei. Coupling constants and chemical shifts are given in Hz and ppm, respectively. The experimental conditions for ¹H (or ¹⁹F) NMR spectra were the following: flip angle 90° (30°), acquisition time 4.5 s (0.7 s), pulse delay 2 s (5 s), number of scans 16 (64), and a pulse width of 5 μs for ¹⁹F NMR.

Infrared spectra were recorded by a Nicolet 510P Fourier Transformed spectrometer from KBr pellets and the intensities of the absorption bands were noted as s = strong, m = medium and w = weak, given in cm⁻¹ (accuracy ± 2 cm⁻¹).

Differential scanning calorimetry (DSC) measurements were conducted using a Perkin-Elmer Pyris 1 instrument connected to a micro-computer. The apparatus was calibrated with indium and n-decane. After its insertion into the DSC apparatus, the sample was initially cooled to -105°C for 15 min. Then, the first scan was made at a heating rate of 40°C.min⁻¹ up to 80°C, where it remained for 2 min. It was then cooled to -105°C at a rate of 320°C.min⁻¹ and left for

10 min at that temperature before a second scan was started at a heating rate of $20^{\circ}\text{C}.\text{min}^{-1}$. Finally, another cycle was performed and a third scan at a heating rate of $20^{\circ}\text{C}.\text{min}^{-1}$ was initiated, giving the values of T_g reported herein, taken at the half-height of the heat capacity jump of the glass transition.

Thermogravimetric analyses were performed with a Texas Instrument TGA 51-133 apparatus in air at a heating rate of $10^{\circ}\text{C}.\text{min}^{-1}$ from room temperature up to a maximum of 600°C .

The synthesized copolymers were characterized by size exclusion chromatography (SEC) carried out in tetrahydrofuran at 30°C , at a flow rate of 0.8 mL/min , by means of a Spectra Physics Winner Station, a Waters Associate R 401 differential refractometer and a set of four columns connected in series: Styragel (Waters) HR4 5μ , HR3 analyses 5μ , PL Gel (Polymer Laboratories) 5μ 100 \AA . Monodispersed poly(styrene) standards were used for calibration. Aliquots were sampled from the reaction medium, diluted with tetrahydrofuran up to a known concentration (ca. 4% wt.-%), filtered through a $20\text{ }\mu\text{m}$ PTFE Chromafil Membrane and finally analyzed by GPC under the conditions described above.

The high frequency resistance of the membrane was measured by the impedance technique⁵²⁻⁵⁴. Using a mercury cell, the variation of the membrane resistance as both a function of its ionic composition and water content can be monitored.

Syntheses of monomers

1-Synthesis of 4-[(α,β,β -trifluorovinyl)oxy] bromo benzene (TFVOBB)

4-[(α,β,β -trifluorovinyl)oxy]bromobenzene was prepared by published method^{43a}. Into a two-necked round bottom flask equipped with a Dean-Stark azeotropic distillation assembly, a reflux condenser and a magnetic stirrer, were introduced, under nitrogen atmosphere, 100.1 g (0.582 mol) of 4-bromophenol, 37.4 g (0.583 mol) of KOH, 320 mL of DMSO, and 80 mL of xylene. The mixture was stirred and heated to 100°C (ca. 200 mmHg) for 48 hours during which time water was removed. The solution was cooled to 30°C , and 166.5 g (0.641 mol) of 1,2-dibromotetrafluoroethane were dropwise added in 4 hours such that the temperature did not exceed 30°C . The mixture was stirred for 16 hours at 22°C , and then 10 hours at 35°C .

The reaction mixture was diluted with H₂O, extracted with methylene chloride and dried with MgSO₄. 4-(2-Bromotetrafluoroethoxy)bromobenzene (**1**) was purified (yield 70 %) from the crude oil by distillation (b.p. = 110-115°C/25 mm Hg). Afterwards, 100 g (0.284 mol) of bromo ether (**1**) was slowly added under nitrogen conditions to a stirring mixture of 18.6 g (0.284 mol) of zinc turnings in 250 mL of acetonitrile at 80 °C. The mixture was refluxed for 24 hours and then the solvent were evaporated. The crude product was extracted from the salts with hexane, concentrated and distilled (bp 65-75 °C, 20 mmHg) giving 57 g (78 %) of 4-[(trifluorovinyl)oxy]bromobenzene. ¹H NMR (250 MHz, CDCl₃) δ: 6.9 (2H, d, ³J_{HH} = 8.8 Hz), 7.4 (2H, d, ³J_{HH} = 8.8 Hz); ¹⁹F NMR (250 MHz, CDCl₃) δ: -119.8 (dd, *cis*-CF=CF₂, F_a, ²J_{FaFb} = 96 Hz, ³J_{FaFc} = 58 Hz, 1F), -126.7 (dd, *trans*-CF=CF₂, F_b, ²J_{FbFa} = 96 Hz, ³J_{FbFc} = 110 Hz, 1F), -134.9 (dd, CF=CF₂, F_c, ³J_{FcFa} = 58 Hz, ³J_{FcFb} = 110 Hz, 1F).

2-Synthesis of 4-[(α,β,β-trifluorovinyl)oxy] benzene sulfonyl chloride (TFVOBSC)

In a two-necked round bottom flask containing a septum and a nitrogen purge, 22.802 g (0.091 mol) of TFVOBB and 50 mL of diethyl ether were introduced under nitrogen atmosphere, then cooled at -80°C. To this mixture 50 mL of 1.7 M *t*-butyl lithium (in hexane) (0.088 mol) was dropwise added over 45 minutes and additionally stirred for 2 hours while maintaining the temperature at -80°C. This lithium reagent was added dropwise, using vacuum/nitrogen flow techniques, through a double ended needle into a separate two-necked round bottom flask containing 50 mL of ether and 15 g of SO₂Cl₂ (0.11 mol) also maintaining at -80°C. The reaction mixture was stirred for 30 minutes at -80°C. At this time 100 mL of deionized water was added to the reaction forming an organic and an aqueous layers. The two layers were separated. TFVOBSA was dried over MgSO₄ and purified by vacuum distillation (b.p. = 116-121°C/0.1 bar) and obtained in 68 % yield (purity 90 %). ¹H NMR (250 MHz, CDCl₃) δ: 7.1-7.3 (m, ArH, 2H), 7.9-7.1 (m, ArH, 2H); ¹⁹F NMR (250 MHz, CDCl₃) δ: -117.8 (dd, *cis*-CF=CF₂, F_a, ²J_{FaFb} = 98 Hz, ³J_{FaFc} = 55 Hz, 1F), -124.7 (dd, *trans*-CF=CF₂, F_b, ²J_{FbFa} = 98 Hz, ³J_{FbFc} = 117 Hz, 1F), -136.1 (dd, CF=CF₂, F_c, ³J_{FcFa} = 55 Hz, ³J_{FcFb} = 117 Hz, 1F). FTIR: 1196 (s, C-F stretch), 1381 (s, O=S=O stretch).

3-Synthesis of 4-[(α,β,β -trifluorovinyl)oxy] benzene sulfonic acid (TFVOBSA)

Into a two-necked round bottom flask equipped with a reflux condenser and a magnetic stirrer was charged under a nitrogen atmosphere 18.005 g (0.070 mol) of TFVOBSC. 280 mL of a solution of KOH in methanol (0.5 M) was added dropwise to the mixture at room temperature for 2 hours. The mixture was allowed to stir for 12 hours. At this time, the salts were filtered off and the solvent was evaporated under vacuum. TFVOBSA was extracted (yield 88 %) from the crude oil by distillation under vacuum (b.p. = 119-125°C/5 mm Hg). ^1H NMR (250 MHz, CDCl_3) δ : 7.4-7.6 (m, ArH, 2H), 8.0-8.2 (m, ArH, 2H); ^{19}F NMR (250 MHz, CDCl_3) δ : -115.1 (dd, *cis*-CF=CF₂, F_a, $^2J_{\text{FaFb}}$ = 102 Hz, $^3J_{\text{FaFc}}$ = 59 Hz, 1F), -122.2 (dd, *trans*-CF=CF₂, F_b, $^2J_{\text{FbFa}}$ = 102 Hz, $^3J_{\text{FbFc}}$ = 109 Hz, 1F), -137.1 (dd, CF=CF₂, F_c, $^3J_{\text{FcFa}}$ = 59 Hz, $^3J_{\text{FcFb}}$ = 109 Hz, 1F). FTIR: 3373 and 1029 (s, S(O)(OH)₂ stretch), 1000-1300 (s, C-F stretch).

Terpolymerization

The batch terpolymerizations of VDF, HFP or PMVE with TFVOBSC were performed in a 160 ml HASTELLOY (HC 276) autoclave, equipped with a manometer, a rupture disk, an inlet valve. This vessel was left closed for 20 minutes and purged with 20 bars of nitrogen pressure to prevent any leakage, and degassed afterwards. Then, a 20 mm Hg vacuum was operated for 15 min and the initiator (2,5-Bis(*tert*-butylperoxy)-2,5-dimethylhexane, tech, 90% : $C_0 = ([2,5\text{-Bis}(\textit{tert}\text{-butylperoxy})\text{-}2,5\text{-dimethylhexane}] / \Sigma[\text{Monomers}]) = 0.9 \text{ mol } \%$), TFVOBSC, and 1,1,1,3,3-pentafluorobutane were introduced successively via a funnel tightly connected to the introduction valve. Next, HFP or PMVE, and VDF were respectively introduced by double weighing. The autoclave was then heated up to 134°C for 10 hours. After reaction, the vessel was cooled to room temperature and then put in an ice bath. Then, the crude product was analyzed by ^{19}F NMR spectroscopy. The solvent was evaporated and the crude product was solubilized in DMF and then precipitated from cold water. The precipitate was filtered off and dried over P₂O₅ agent at room temperature under a 20 mm Hg vacuum for 48 hours.

Hydrolysis of the terpolymers containing TFVOBSC units

10 g of terpolymers incorporating VDF, HFP or PMVE, and TFVOBSC were placed in a 50 mL flask and stirred with 25 mL of acetone. To this solution were added dropwise, at room temperature a solution of KOH in MeOH (0.5 mol/L) with a 1.0 equivalent molar ratio. After the addition, the solution was allowed to stir for 1 hour. Afterwards, the excess of basic solution was neutralized by HCl since the pH goes under 7. The solution was filtered, the solvent was evaporated, and then precipitated from cold water. The precipitate was filtered off and dried over P_2O_5 agent at room temperature under a 20 mm Hg vacuum for 48 hours.

Preparation of the membranes by casting

The terpolymers containing VDF, HFP or PMVE, and TFVOBSA (70 wt. %), and a commercial poly(VDF-*co*-HFP) copolymer (3M) (30 wt. %) were placed in a 50 mL flask and stirred with NMP for 1 hour at 45 °C. Afterwards, the mixture was sprayed on a Teflon[®] substrate, and the solvent was evaporated using a heating table at 40 °C. These casted membranes were removed from the substrates in the presence of water. The average thicknesses were ranging between 60 and 80 μm .

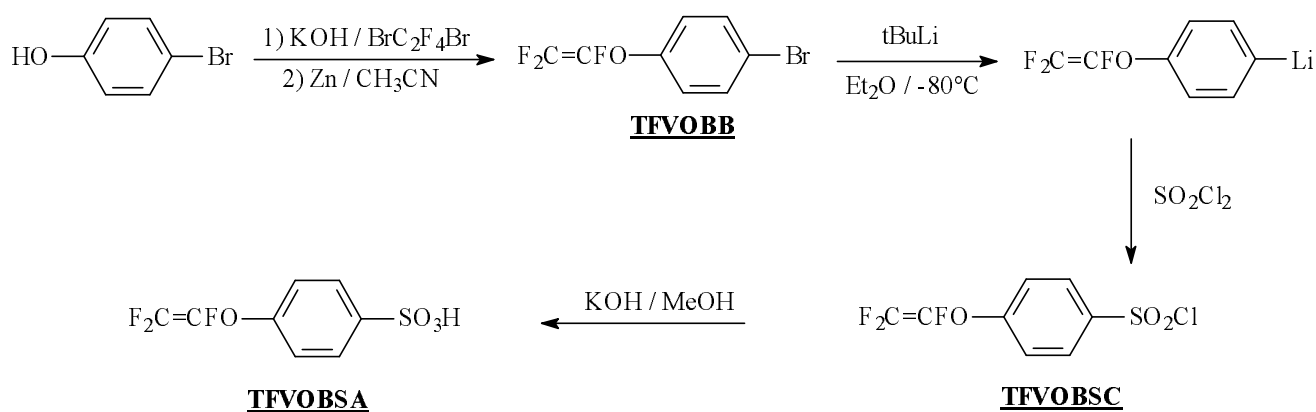
Results and discussion

The elaboration of the membranes was carried out in three steps. This first section seeks to report the synthesis of 4-[(α,β,β -trifluorovinyl)oxy] benzene sulfonyl chloride (TFVOBSC). The second part covers the terpolymerization of TFVOBSC with fluoroalkenes. The physico-chemical properties of the terpolymers are discussed. The third part is devoted to the hydrolysis of these fluorinated macromolecules was achieved and the proton exchange membranes were obtained by casting. Finally, the properties of membranes are presented.

(I) Synthesis of monomers

First the synthesis and the characterization of 4-[(α,β,β -trifluorovinyl)oxy] benzene sulfonyl chloride (TFVOBSC) were investigated.

4-[(α,β,β -trifluorovinyl)oxy] bromo benzene (TFVOBB) synthesis was previously reported in 1996 by Smith *et al.*^{43a} and is based on a nucleophilic substitution of 4-bromophenolate to 1,2-dibromotetrafluoroethane followed by a dehalogenation reaction (Scheme 1).



Scheme 1: Synthesis and hydrolysis of 4-[(α,β,β -trifluorovinyl)oxy] benzene sulfonyl chloride (TFVOBSC)

Afterwards, we focused on a novel synthetic route to prepare 4-[(α,β,β -trifluorovinyl)oxy] benzene sulfonic acid (TFVOBSA). Ford *et al.*^{13,44} investigated the synthesis of 4-[(α,β,β -trifluorovinyl)oxy] benzenesulfonyl chloride (TFVOBSC), obtained in a 65 % yield, by using

sulfonyl chloride fluoride (FSO₂Cl) as one of the reactants. We propose a new way to synthesize TFVOBSC. Interestingly, we have found that the organolithium intermediate of TFVOBB^{41,44-46} reacted with SO₂Cl₂ at –80 °C (Scheme 1) yielding TFVOBSC in a better yield (72 %) than that previously reported⁴⁴.

TFVOBSA was obtained, in 88 % yields, from a basic hydrolysis of TFVOBSC in the presence of KOH and methanol (Scheme 1).

TFVOBSC and TFVOBSA were characterized by ¹H, and ¹⁹F NMR, and IRTF (Table 3). The ¹H NMR spectra of these monomers show multiplets centered between 7.2 and 8.1 ppm, characteristic of the aromatic protons. ¹⁹F NMR spectra exhibit three doublet of doublets centered at –117.8, 124.7 and 136.1 ppm characteristic of F_a, F_b and F_c atoms, respectively (Table 3). For TFVOBSA, we note a slightly difference on the chemical shifts in the ¹H, and ¹⁹F NMR induced by electron-withdrawing of the para-group.

Insert Table 3

(II) Radical terpolymerizations of TFVOBSC with fluoroalkenes

This section covers the synthesis of original fluorinated terpolymers incorporating TFVOBSC obtained in radical conditions. The physico-chemical properties of the materials are reported.

II-1 Radical (co)polymerization of aryl α,β,β-trifluorovinyl ether

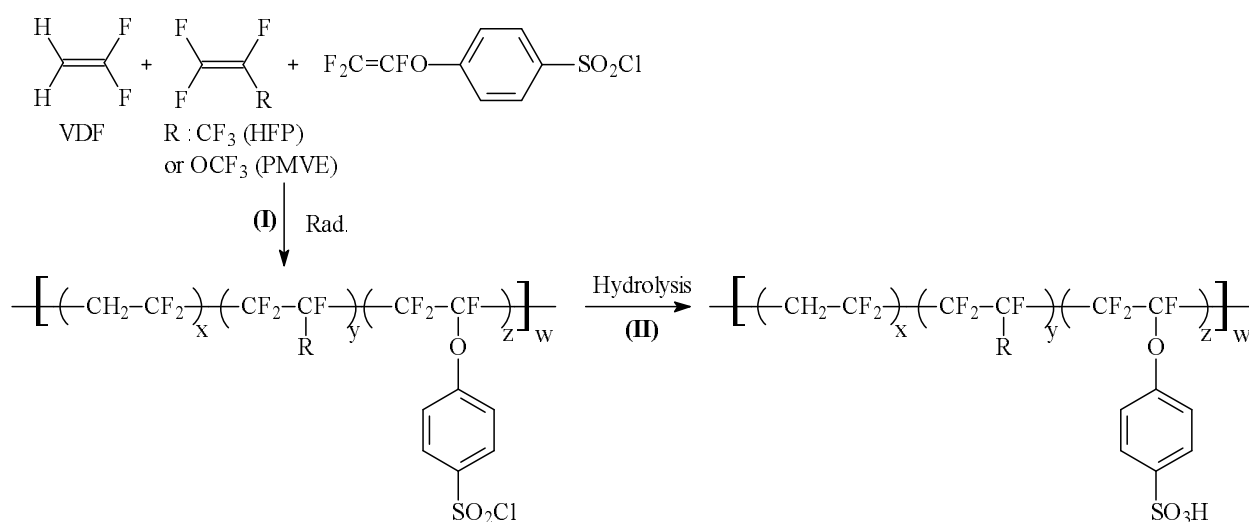
In a previous work, a model of radical (co)polymerization of aryl α,β,β-trifluorovinyl ether was achieved⁴⁷. [(α,β,β-Trifluorovinyl)oxy]bromobenzene (TFVOBB) was used as a model monomer. First, it has been showed that aryl α,β,β-trifluorovinyl ether do not homopolymerize under radical initiation but thermocyclodimerize $[2\pi + 2\pi]$ ^{21,23a,23b,38,42-43,47}. Furthermore, this study showed that the copolymerization with commercially available fluoroalkenes, initiated by 2,5-bis(*tert*-butylperoxy)-2,5-dimethylhexane led to better massic yields. The radical polymerization has been performed in 1,1,1,3,3-pentafluorobutane because of its lower transfer activity on the growing macroradical than that of acetonitrile⁴⁸. In order to enhance the reactivity of VDF, a termonomer like hexafluoropropene (HFP), or perfluoromethyl vinyl ether (PMVE) was also introduced. A series of terpolymerization of aryl vinyl ethers with VDF, and HFP (or PMVE) was investigated, and the microstructures of

the products (i.e., the molar percentages of each termonomers in the terpolymers) were characterized by ^1H and ^{19}F NMR spectroscopies. It has been demonstrated that the ^{19}F NMR signals centered at -113.5 and -124.5 ppm would be assigned to the difluoromethylene group and the tertiary fluorine of a α,β,β -trifluorovinyl ether respectively⁴⁷. The results of the incorporation content of each terolefin are gathered in Table 4. Finally, it appears that the incorporation of α,β,β -trifluorovinyl ether in the terpolymer is enhanced in the VDF/PMVE system which is better than that in the VDF/HFP.

Insert Table 4

II-2 Radical terpolymerization of TFVOBSC

Our initial goal was to produce materials incorporating TFVOBSC units. As a matter of fact, we used former results described above since it can be assumed that the influence of chlorosulfonyl function (SO_2Cl) is similar to that of bromine atom. Because of the low incorporation rates obtained in the study described above, the radical copolymerization of TFVOBSC with VDF was not attempted. Hence, the radical terpolymerizations of these functional aromatic monomers with VDF and / or HFP and / or PMVE were investigated (Scheme 2).



Scheme 2: Radical terpolymerization (I) of TFVOBSC with VDF and / or HFP and / or PMVE, and hydrolysis (II) of the corresponding terpolymers⁴⁰.

Using the optimal experimental conditions of terpolymerization of TFVOBB with the fluoroalkenes above, we have decided to perform all following experiments in solution in 1,1,1,3,3-pentafluorobutane initiated by 2,5-bis(*tert*-butylperoxy)-2,5-dimethylhexane. After reaction, the resulting fluorinated macromolecules were precipitated from cold pentane and the materials were characterized by ^1H and ^{19}F NMR, and IR spectroscopies which enabled us to characterize the microstructure of these terpolymers and the specific functions.

In all cases, statistic terpolymers were obtained in which microblocks of oligo(VDF)s were noted in the terpolymer. The amounts of monomer units in the terpolymers were assessed by ^{19}F NMR. In addition, all ^1H NMR spectra exhibit: (i) the signals assigned to methylene groups of VDF units adjacent to difluoromethylene groups in the 3.0-3.4 ppm range (including the “head-to-head” and “head-to-tail addition” in the oligo(VDF) chain) and (ii) the signals attributed to aromatic groups at about 7.6 ppm. Interestingly, the absence of triplet of triplet centered at 6.1 ppm in the ^1H NMR spectra, and that of the multiplet at -114.8 ppm in ^{19}F NMR spectra, characteristic of $-(\text{CH}_2\text{CF}_2)-\text{CH}_2\text{CF}_2\text{H}$ were observed. Hence, the transfer reaction onto the macroradical can be eliminated.

Insert Figure 1

II-2-1) Terpolymerization of TFVOBSC with VDF and HFP

The ^{19}F NMR spectroscopy was chosen as the method to identify the corresponding TFVOBSC, VDF, and HFP contents in the terpolymers.

First, this spectrum (Figure 2 and Table 5) shows a signal centered at -91.3 ppm (noted $I_{91.3}$) assigned to the difluoromethylene groups characteristic of the head-to-tail VDF addition. Furthermore, a series of other signals centred at -95.1 (noted $I_{95.1}$), -113.7 (noted $I_{113.7}$) and -115.6 (noted $I_{115.6}$) ppm are assigned to the CF_2 groups in $(\text{CH}_2-\text{CF}_2)-(\text{CF}_2-\text{CH}_2)-(\text{CH}_2-\text{CF}_2)-(\text{CH}_2-\text{CF}_2)$; $-(\text{CH}_2-\text{CF}_2)-(\text{CF}_2-\text{CH}_2)-(\text{CF}_2-\text{CH}_2)-$; $-(\text{CH}_2-\text{CF}_2)-(\text{CF}_2-\text{CH}_2)-(\text{CH}_2-\text{CF}_2)-$ sequences, respectively. They are attributed to the head-to-head VDF reverse addition. Furthermore, it was observed the peaks located at -109.7 ppm (noted $I_{109.7}$) and -110.2 (noted $I_{110.2}$) are assigned to the difluoromethylene groups of the VDF unit adjacent to HFP and TFVOBSC unit, respectively.

In addition, the chemical shifts centered at -70.9 (noted $I_{70.9}$), -74.9 (noted $I_{74.9}$) are assigned

to the trifluoromethyl side group of HFP in the terpolymer, while those centered at -118.7 (noted $I_{-118.7}$) and -184.1 (noted $I_{-184.1}$) ppm are attributed to the difluoromethylene groups and to the tertiary fluorine in HFP, respectively. These expected chemical shifts confirmed previous works^{47,49}.

Finally, the multiplet centered at -113.8 ppm (noted $I_{-113.8}$) is attributed to the difluoromethylene of TFVOBSC unit in the terpolymer : $-(CF_2-CF(O-Ph-SO_2Cl))-$. The peaks located in the -123.5 to -125.5 ppm region (noted $I_{-124.7}$) are assigned to the tertiary fluorine atom in the CF group of TFVOBSC, as observe in the copolymers containing TFVOBB⁴⁷.

Insert Table 5

Insert Figure 2

From the ^{19}F NMR spectra, the determination of the molar fractions of VDF, HFP and TFVOBSC units in the terpolymer was achieved and is given by the following equations (Eq. 1):

$$\text{Mol \% of VDF in the terpolymer} = \frac{I_A}{I_A + I_B + I_C} \times 100 \quad (\text{Eq. 1a})$$

$$\text{Mol \% of HFP in the terpolymer} = \frac{I_B}{I_A + I_B + I_C} \times 100 \quad (\text{Eq. 1b})$$

$$\text{Mol \% of TFVOBSC in the terpolymer} = \frac{I_C}{I_A + I_B + I_C} \times 100 \quad (\text{Eq. 1c})$$

$$\text{with: } I_A = \frac{I_{-91.3} + I_{-95.1} + I_{-109.8} + 2 \times I_{-115.7}}{2}$$

$$I_B = \frac{I_{-70.9} + I_{-74.9}}{3}$$

$$I_C = \frac{I_{-113.8} + I_{-115.7}}{2}$$

The incorporation percentages of each monomer in the terpolymers are listed in Table 6.

Insert Table 6

II-2-2) Terpolymerization of TFVOBSC with VDF and PMVE

The ^{19}F NMR spectrum (Figure 3) of the poly(VDF-*ter*-PMVE-*ter*-TFVOBSC) shows the presence of signals characteristic of the difluoromethylene groups of VDF addition and

centered at about -91.1, -94.3, -113.1, and -115.8 ppm, noted $I_{-91.1}$, $I_{-94.3}$, $I_{-113.1}$, and $I_{-115.8}$, respectively, as in the example above. In addition, the signals located in the -110.1 to -110.8 ppm range are assigned to the difluoromethylene groups of the VDF unit adjacent to a PMVE (noted $I_{-110.1}$) and TFVOBSC (noted $I_{-110.8}$) unit, respectively. Furthermore, the chemical shifts centered at -48.3 and -52.1 (noted $I_{-48.3}$ and $I_{-52.1}$) assigned to the trifluoromethyl side group, -120.8 ($I_{-120.8}$), and -122.2 ($I_{-122.2}$) characteristic of the difluoromethylene groups, and -125.4 ($I_{-125.4}$) and -145.3 ($I_{-145.3}$) which are assigned to the tertiary fluorine of PMVE. These expected chemical shifts are in good agreement with those noted for the copolymers of VDF and PMVE⁴⁷. Finally, the peaks centered at -113.4 ($I_{-113.4}$) and -125.2 ($I_{-125.2}$) ppm are attributed to the difluoromethylene group and tertiary fluorine atom the of TFVOBSC unit in the terpolymer respectively (Table 7).

Hence, the molar percentages of VDF, PMVE and TFVOBSC in the terpolymers can be assessed from equation 2, and the results of incorporation are gathered in Table 6.

$$\text{Mol \% of VDF in the terpolymer} = \frac{I_D}{I_D + I_E + I_F} \times 100 \quad (\text{Eq. 2a})$$

$$\text{Mol \% of PMVE in the terpolymer} = \frac{I_E}{I_D + I_E + I_F} \times 100 \quad (\text{Eq. 2b})$$

$$\text{Mol \% of TFVOBSC in the terpolymer} = \frac{I_F}{I_D + I_E + I_F} \times 100 \quad (\text{Eq. 2c})$$

with:

$$I_D = \frac{I_{-91.1} + I_{-94.3} + I_{-110.1} + I_{-110.8} + 2 \times I_{-115.8}}{2}$$

$$I_E = \frac{I_{-48.3} + I_{-52.1}}{3}$$

$$I_F = \frac{I_{-113.4} + I_{-115.8}}{2}$$

Insert Figure 3

Insert Table 7

First, and as expected, the VDF content in the terpolymers is higher than that in feed. In the VDF / HFP / TFVOBSC terpolymerization, the results listed in Table 6 showed that the

presence of TFVOBSC monomer made decreasing the yields by mass. In the same experimental conditions, starting from TFVOBSC feed molar percentages of 3.4 and 4.8 mol % led to terpolymers containing 3.6 and 6.7 mol %, respectively. Furthermore, above a certain feed concentration of TFVOBSC (> 7 mol %), a drastic decrease of the overall yields was observed. As a matter of fact, the higher the TFVOBSC in feed, the lower the yields by mass.

II-2-3) Physico-chemical properties of terpolymers incorporating TFVOBSC

The SEC measurements were not quite accurate because of the lack of standards for poly(VDF-co-HFP). Nevertheless, these analyses showed that the value of the molecular weight of the terpolymer synthesized in experiment 7 (2.9 mol % in feed of TFVOBSC) is higher than that of experiment 8 (6.1 mol % in feed of TFVOBSC). From these results, several hypotheses can be formulated: (i) a strong interaction between the aromatic ring of TFVOBSC and macroradicals (ii) the low reactivity of \sim TFVOBSC \cdot macroradical, (iii) the inhibition of TFVOBSC monomer in the radical terpolymerization (due to a possible transfer of the chlorine atom on the macroradical which yet was not observed in the TFVOBB radical terpolymerization), (iv) and the possible cyclodimerization of two \sim TFVOBSC \cdot macroradicals. Having these results, two experiments were achieved in the VDF / PMVE / TFVOBSC system. The structure and physico-chemical properties observed (see Table 6) confirmed the last hypothesis.

Furthermore, glass transition temperature (Tgs) were assessed by Differential scanning calorimetry analyses. Poly(VDF-*ter*-HFP-*ter*-TFVOBSC) terpolymers exhibit Tgs ranging between -21 and -30 °C as evidenced of fluoroelastomers. Experiment 9 exhibited the lowest Tg, and is due to the fact that the prepared fluorinated macromolecules incorporated a high amount of VDF (i.e., $T_{g \text{ PVDF}} = -35^{\circ}\text{C}$). Furthermore, the Tgs increases with the molar percentages of TFVOBSC in the terpolymer, which confirmed a previous studies⁴⁷. For VDF/PMVE/TFVOBSC system, the noted Tgs are very low and are characteristics of a (co)polymer incorporating perfluoromethyl vinyl ether⁵⁰.

In addition, the thermal analyses (Figure 4) of two poly(VDF-*ter*-HFP-*ter*-TFVOBSC) terpolymers (experiments 7 and 8) indicate that the copolymer prepared in experiment 7 is more thermostable than that synthesized in experiment 8, which involved the highest mol % of TFVOBSC in the terpolymer. As a matter of fact, the higher the mol % of VDF in the

terpolymer the higher its thermostability. Figure 4 shows 2 TGA curves which showed three steps: (i) the first one corresponds to the desulfoxydation and the elimination of O-Ph group ($280 < T < 320$ °C), (ii) the second one is attributed to the dehydrofluorination ($340 < T < 460$ °C), (iii) from $T > 500$ occurs the backbone degradation.

Insert Figure 4

Interestingly, the comparison of Tables 4 and 6 showed that TFVOBSC is less reactive than TFVOBB in radicalar terpolymerization with VDF / HFP or VDF / PMVE. These low incorporation percentages and the yields by mass could be explained by the effect of the aromatic ring which could undergo side reactions with the growing macroradicals.

(III) Preparation and characterization of proton exchange membranes

In this part, the basic hydrolysis of the poly(VDF-*ter*-HFP-*ter*-TFVOBSC) and poly(VDF-*ter*-HFP-*ter*-TFVOBSC) terpolymers and the membrane formulation are discussed. Four main characteristics of the membranes are presented: (i) the ionic exchange capacity, (ii) the thermal stability, (iii) the swelling rates, (iv) and the proton conductivity.

*III-1 Synthesis of ionomers based on hydrolysis of poly(VDF-*ter*-HFP-*ter*-TFVOBSC) and poly(VDF-*ter*-HFP-*ter*-TFVOBSC) terpolymers*

A hydrolysis reaction of the terpolymers prepared above was required to obtain sulfonic acid groups. TFVOBSC units were then successfully hydrolyzed in the corresponding sulfonic acids by using potassium hydroxide in methanol. The overall yields were quantitative. In all cases ^1H and ^{19}F NMR analysis of the modified terpolymers indicate that the backbone of the macromolecules were not degraded by the basic treatment, especially VDF units known to be base sensitive (absence of signals in the 5 – 6.5 ppm range in ^1H NMR spectra). Furthermore, the IR spectra of hydrolyzed materials exhibited absorptions at 3377 and 1026 cm^{-1} due to the $\text{S}(\text{O})(\text{OH})_2$ stretching vibrations of the sulfonic acid groups. As a matter of fact, the absorption signals centered at 1381 cm^{-1} , characteristic of the $\text{O}=\text{S}=\text{O}$ stretching vibration of the chlorosulfonyl groups were absent.

Since the end of the study, we will investigate the synthesis and the characterizations of PEMFC based on hydrolyzed terpolymers arising from experiments 7, 8, and 10 (they will be

noted ionomers A, B, and C, respectively). Furthermore, the SEC chromatograms showed that the average molecular weights in number of the terpolymers were slightly modified by that hydrolysis, and differential scanning calorimetry demonstrated also that the hydrolysis of sulfonyl chloride end groups enabled these T_g values of the terpolymers to be slightly increased (-15, -7, and -19 °C for ionomers A, B, and C, respectively). The TGA thermograms showed a similar thermostability than those observed for non hydrolyzed terpolymers prepared above, and confirmed also the presence of sulfonic acids by the presence of a degradation step at 330 °C characteristic of the desulfoxydation of sulfonic acids⁵¹.

III-2 Fuel cell membranes of ionomers A, B, and C: synthesis and characterization

III-2-1 Choice of the solvent for casting membranes

This part deals with the preparation of membranes from ionomers synthesized above. Two main factors were studied to formulate the above fluoropolymer into membranes by casting: the nature and the amount of solvent and the ionomer / commercially available fluoropolymer ratio.

The first one deals with the nature of the solvent. Solvents are used in membranes formulation to thin the film, to affect application, flow, and final uniformity of the membrane on the substrate. Through this relatively simple statements, selecting solvents is really complex. It is unusual for one solvent to successfully provide all the desirable properties. The solvent must be compatible with the ionomer and must have chemical properties that will not adversely affect the film or harm the substrate. Solvents for the formations of fluoropolymer film can be divided into four different classes: (i) the active solvents, because they may totally dissolve or partially dissolve fluoro-ionomers at room temperature ; (ii) the latent or intermediate solvents, because they do not dissolve or swell materials at room temperature (working at elevated temperatures is necessary) ; (iii) the non-solvent, which do not dissolve fluoropolymers up to their boiling points.

In our study, experiments have been achieved using acetone, N-methylpyrrolidinone (NMP), dimethylacetamide (DMAC), and dimethyl formamide (DMF) which are active solvents.

The second one is the ratio between the commercially available fluoropolymers that is used in the membrane. A series a formulation was investigated with a ionomer / commercially available poly(VDF-co-HFP) copolymer, the mass ratio ranging between 95 / 5 and 10 / 90. From this study, it has been shown that membranes of ionomers formulated in NMP with a ratio by mass of 70 / 30 (ionomer / commercially poly(VDF-co-HFP)) had the best film forming properties (regarding the homogeneity, the color, and the texture). Furthermore, DSC analysis of those membranes showed only one glass transition temperature, which is characteristic of a good miscibility between the ionomer and the commercially copolymer.

III-2-2 Properties of the membranes

This section reports the characterization of the membranes prepared above, and incorporating ionomers A, B or C. Various properties were investigated such as the ionic exchange capacity (IEC), the thermal stability, the swelling rates, and the proton conductivity.

a) Ionic exchange capacity

The IECs (mEq H⁺ / g) of the membranes representing the number of protonic groups for 1 g of terpolymer were determined. It was required the calculated, the molar ratios of each termonomer (VDF, HFP or PMVE, and TFVOBSA) from ¹⁹F NMR (see Eq. 1 and 2). Hence, the ionic exchange capacity can be assessed from equation 3, and the results are gathered in Table 8 (knowing that molecular weights of VDF, HFP, PMVE and TFVOBSA are 64, 150, 166, 254 g / mol, respectively).

$$x \text{ (from scheme 2)} = \frac{\text{Mol \% of VDF in the terpolymer}}{100} \quad (\text{see Eq. 1a or 2a})$$

$$y \text{ (from scheme 2)} = \frac{\text{Mol \% of HFP or PMVE in the terpolymer}}{100} \quad (\text{see Eq. 1b (HFP) or 2b (PMVE)})$$

$$z \text{ (from scheme 2)} = \frac{\text{Mol \% of TFVOBSA in the terpolymer}}{100} \quad (\text{see Eq. 1c or 2c})$$

For a poly(VDF-ter-HFP-ter-TFVOBSA) terpolymer:

$$\text{IEC (Eq/g)} = \frac{1}{\frac{x}{z} \times 64 + \frac{y}{z} \times 150 + 254} \quad (\text{Eq. 3a})$$

For a poly(VDF-*ter*-PMVE-*ter*-TFVOBSA) terpolymer:

$$\text{IEC (Eq/g)} = \frac{1}{\frac{x}{z} \times 64 + \frac{y}{z} \times 166 + 254} \quad (\text{Eq. 3b})$$

Insert Table 8

The IEC results (Table 8) were ranging between 0.4 and 0.6 mEq H⁺ / g, and as expected, the higher the mol percentages of sulfonic functions in the terpolymer, the higher the IEC. However, the values are lower than that of Nafion[®] 117 (0.9 mEq H⁺ / g)⁵¹.

b) Thermal stability

Furthermore, the thermal properties (T_{gs} and T_{dec}) of these membranes were studied. Surprisingly, the Tg values are still negative in spite of the presence of sulfonic acids (ranging between -25 and -14°C). This can be explained by the fact that our membranes are co-formulated with a very low Tg commercially available poly(VDF-co-HFP) fluoropolymer. As a matter of fact, the resultant Tg was in the low temperature range. Furthermore, the characterization of the decomposition temperature (Td), by TGA under air, showed that our membranes prepared from ionomers A, B, and C exhibit a good thermal stability (up to 300 °C, in all cases). Interestingly, thermograms indicated four different thermal degradation steps: the first one attributed to the loss of water (T<120°C) because of the good affinity of these terpolymers containing sulfonic acid and water, the second one was noted in the 300 °C range and corresponding to the desulfoxidation, a third one characteristic of the dehydrofluorination (400 °C), and the last one in the 500 °C range characteristic of the backbone degradation.

c) Swelling rates

In addition, the swelling rates of the ionomer membranes were also calculated (See equation 4) after immersing the membranes in water for 16 hours. The values of swelling rates, listed in Table 8, ranging between 40 and 90 %, confirmed the presence of the sulfonic acids in the material. As expected, the higher the IEC, the higher the calculated swelling rate.

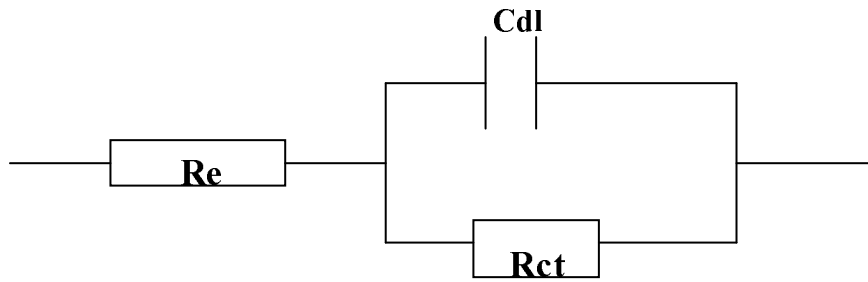
$$\text{Swelling rates (\%)} = \frac{M_1 - M_0}{M_0} \times 100 \quad (\text{Eq. 4})$$

M_0 : weight of the membrane dried for 16 hours at 60 °C

M_1 : weight of the membrane after immersing in water during 24 hours

d) Proton conductivity

The next goal was to assess the corresponding proton conductivity values. An Electrode / Membrane / Electrode can be considered to an electric assembly as following described:



Re: electrolyte resistance

Rct: charge transfert resistance

Cdl: double layer capacity

The complex impedance⁵²⁻⁵⁴, Z , of the electric assembly is given by the following equations (Eq. 5):

$$Z = Z' + jZ'' \quad (Z': \text{real part} ; Z'': \text{imaginary part})$$

$$Z = \frac{R_e + R_{ct}}{1 + jR_{ct}C_{dl}\omega} \quad (\text{Eq. 5})$$

The impedance results are illustrated by plots of the imaginary part of the membrane impedance, Z'' , versus the real part Z' (Nyquist diagram)^{54c}. The value of R_e resistance is measured when $Z'' = 0$.

The values of the membrane resistance deduced from the Nyquist diagram enables the calculation of the proton conductivity of the membrane, σ (S / cm), from the relation (Eq. 6):

$$\sigma = \frac{1}{R_e} \times \frac{e}{S} \quad (\text{Eq. 6})$$

R_e : electrolyte resistance

e : thickness

S: electrode / membrane - surface

The values of σ , gathered in Table 8, and ranging between 0.01 and 0.1 mS.cm⁻¹, are growing up with the IEC. Although the conductivities are low, these encouraging values needs to be optimized, compared to that of Nafion[®] (DuPont) (≈ 100 mS.cm⁻¹). This could be possible by increasing the IEC (i.e., the incorporation percentages of TFVOBSC in the ionomers and increasing the ionomer content in the fluoropolymer blend) or by making polymers which would have higher molecular weights than those prepared above. As a matter of fact, PEMFC could be prepared without poly(VDF-*co*-HFP).

Conclusion

The goal of this study was to prepare original aromatic PEMFC⁴⁰ incorporating fluoroalkenes such as VDF, HFP, and PMVE, with functional aromatic perfluoro vinyl ether. First, TFVOBSC was synthesized in a 72 % overall yields, via a new synthetic route using reactants which were not used in previous study^{13,44}. This monomer exhibits a sulfonyl chloride function, quantitatively hydrolysed into the corresponding sulfonic acid. Original fluorinated aromatic copolymers bearing sulfonic acid side groups were obtained by optimized conditions of terpolymerization in solution. It has been showed that the incorporation of TFVOBSC was not as good as that of the brominated homologue (TFVOBB). We worked with an aromatic monomers to lower the pKa of the sulfonic acids. The poor reactivity of TFVOBSC in radical terpolymerization is still not well-understood and deeper experiments are required. But, the aromatic ring may have reacted with macroradicals inducing low incorporation rates of the functional monomers. Poly(VDF-*ter*-HFP-*ter*-TFVOBSC) and Poly(VDF-*ter*-PMVE-*ter*-TFVOBSC) were hydrolyzed by basic treatment without changing the content of fluoromonomers in the terpolymers. Moreover, membranes were formulated with a commercially available fluoropolymer by casting and led to good film-forming properties. The IEC values were ranging between 0.4 and 0.6 mEq/g, the corresponding protonic conductivities and swelling rates were characterized and the thermal properties studied. It indicates that our materials incorporated sulfonic acids. Although conductivity values are still low. Nevertheless, the properties of these membranes require to be improved for PEMCF applications. In order to improve the electro-chemical properties, these original membranes may be formulated without any commercially available fluoropolymer. It would be necessary to prepare higher molecular weight terpolymers obtained by other polymerization processes (emulsion, suspension, supercritical CO₂). Although, these results seem encouraging in the research of new materials for PEMFC.

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TABLE CAPTIONS:

Table 1: non-fluorinated polymers used in PEMFC

Table 2: Fluoropolymers used in PEMFC

Table 3: Chemical shifts and IR frequencies of $[(\alpha,\beta,\beta\text{-trifluorovinyl})\text{oxy}]$ benzene functionalized by halogenosulfonyl or sulfonic acid groups.

Table 4: Determination of the Monomer/Terpolymer composition of VDF/Terolefin/ TFVOBB *versus* the reaction conditions in the radical terpolymerization of VDF, Terolefin (HFP or PMVE) with TFVOBB. Terpolymerization conditions : $[2,5\text{-Bis(}tert\text{-butylperoxy)-2,5-dimethylhexane}]_0 / ([\text{VDF}]_0 + [\text{Terolefin}]_0 + [\text{TFVOBB}]_0) = 0.9$ mol %, 134°C, 10 hours⁴⁷.

Table 5: ¹⁹F-NMR assignments of fluorinated groups in the poly(VDF-co-HFP-co-TFVOBSC) terpolymers recorded in deuterated acetone.

Table 6: Determination of the Monomer/Terpolymer composition of VDF/Terolefin/ TFVOBSC *versus* the reaction conditions in the radical terpolymerization of VDF, Terolefin (HFP or PMVE) with TFVOBSC. Terpolymerization conditions : $[2,5\text{-Bis(}tert\text{-butylperoxy)-2,5-dimethylhexane}]_0 / ([\text{VDF}]_0 + [\text{Terolefin}]_0 + [\text{TFVOBSC}]_0) = 0.9$ mol %, 134°C, 10 hours. Average molecular weights, M_n and M_w assessed from SEC with poly(styrene) standards. T_g and T_d were measured by DSC and TGA (under air conditions), respectively.

Table 7: ¹⁹F-NMR assignments of fluorinated groups in the poly(VDF-co-PMVE-co-TFVOBSC) terpolymers recorded in deuterated acetone.

Table 8: membrane characteristics prepared from ionomers A, B, and C.

Table 1: non-fluorinated polymers used in PEMFC

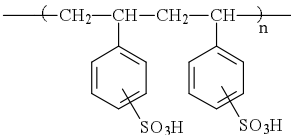
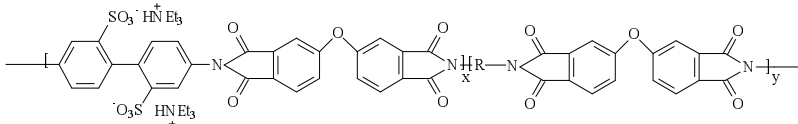
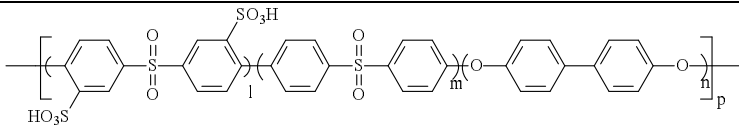
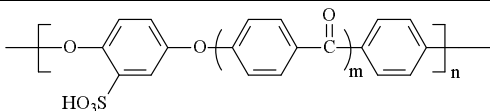
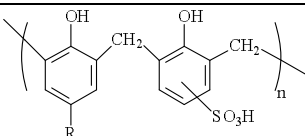
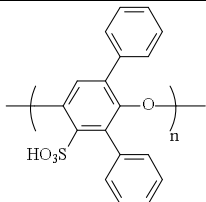
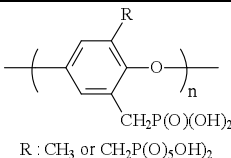
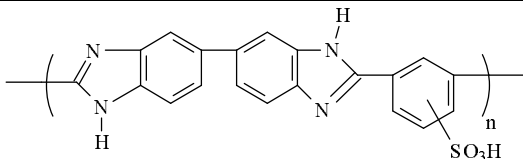
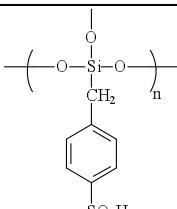
Polymers	Structure	Reference
Sulfonated polystyrenes		[2]
Sulfonated Polyimides		[3]
sulfonated poly(aryl ether sulfones)		[4]
sulfonated poly(aryl ether ketones)		[5]
sulfonated phenol formol resins		[6]
sulfonated Poly(phenylene oxide)		[7]
phosphonic poly(phenylene oxide)		[8]
sulfonated poly(benzimidazole)		[9]
sulfonated silicates		[10]

Table 2: Fluoropolymers used in PEMFC

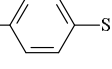
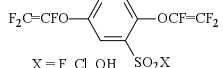
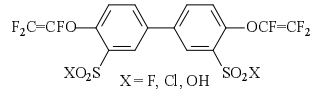
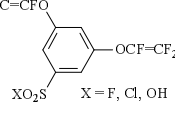
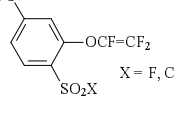
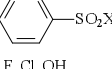
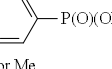

Structure of (Co)polymers	Ref.	Structure of (Co)polymers	Ref.
Copolymer of $\text{Rf-CF=CF-SO}_2\text{F}$ with TFE	[18,20]	$\text{F}_2\text{C=CF-O-C}_3\text{F}_6\text{-P(O)(OEt)}_2$ diethyl perfluoro(3-vinyloxypropyl) phosphonate co- or terpolymerized with TFE and perfluoro (propyl vinyl ether)	[27]
Copolymer of $\text{F}_2\text{C=CF-(OCF}_2\text{CF(CF}_3\text{))}_p\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$ with TFE (p: 0 or 1) Nafion [®] , Flemion [®]	[21]	$\text{F}_2\text{C=CFP(O)(OH)}_2$	[35]
Copolymer of $\text{F}_2\text{C=CF-OCF}_2\text{CF}_2\text{SO}_2\text{F}$ with TFE Dow Chemical Membrane, Hyflon [®] Ion	[1b,22,23 c]	$\text{F}_2\text{C=CF-O-}$  $\text{-SO}_2\text{X}$ X = F, Cl, OH Polymer obtained by thermocyclodimerization	[13]
Copolymer of $\text{F}_2\text{C=CF-CF}_2\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$ with TFE	[24,25]	$\text{F}_2\text{C=CFO-}$  -OCF=CF_2 X = F, Cl, OH Polymer obtained by thermocyclodimerization	[13]
Copolymer of $\text{F}_2\text{C=CF-OCF}_2\text{CF(CF}_3\text{)OCF}_2\text{CF}_2\text{G}$ with TFE G: $\text{SO}_2\text{NH}_2\text{SO}_2\text{CF}_3$, $\text{N(Na)SO}_2\text{CF}_3$ or $\text{N(Na)SO}_2\text{C}_4\text{F}_8\text{SO}_2\text{N(Na)SO}_2\text{CF}_3$	[26]	$\text{F}_2\text{C=CFO-}$  -OCF=CF_2 X = F, Cl, OH Polymer obtained by thermocyclodimerization	[13]
Copolymer of perfluorovinyl ethoxy sulfonyl fluoride with VDF	[27]	$\text{F}_2\text{C=CFO-}$  -OCF=CF_2 X = F, Cl, OH Polymer obtained by thermocyclodimerization	[13]
(Ter)polymer of perfluorosulfonyl fluoride ethoxy propyl vinyl ether (PSEPVE) with VDF and / or HFP	[28-29a, 29b]	$\text{F}_2\text{C=CFO-}$  -OCF=CF_2 X = F, Cl, OH Polymer obtained by thermocyclodimerization	[13]
Copolymer of $\text{F}_2\text{C=CFOCF}_2\text{CF(CF}_3\text{)OC}_2\text{F}_4\text{R}$ with VDF	[30,31] R : NHSO_2CF_3 [28-32] R : $\text{SO}_2\text{CLi(SO}_2\text{CF}_3\text{)}_2$, $\text{SO}_2\text{NLiSO}_2\text{CF}_3$ and SO_2F (PSEPVE) [31]	$\text{F}_2\text{C=CF-}$  $\text{-SO}_2\text{X}$ X: F, Cl, OH Homopolymer or copolymer with Trifluorostyrene	[15a,31]
Copolymer of $\text{F}_2\text{C=CF-COOH}$ with TFE	[27,28,30]	$\text{F}_2\text{C=CF-}$  -P(O)(OR)_2 R: H or Me Homopolymer or copolymer with Trifluorostyrene	[15b]
Copolymer of $\text{H}_2\text{C=CFCF}_2\text{OCF(CF}_3\text{)CF}_2\text{CO}_2\text{CH}_3$ ^{29c} with VDF	[29c]	$\text{F}_2\text{C=CF-O-}$  -G a)G: P(O)(OR)_2 (R: H, Me or Et) b)G: SO_3H Terpolymer with VDF / HFP or VDF / PMVE	a)[40,4 b)this work
Copolymer of $\text{F}_2\text{C=CFOCF}_2\text{CF(CF}_3\text{)OCF}_2\text{CF}_2\text{COOCH}_3$ with TFE	[31]		
Copolymer of $\text{F}_2\text{C=CFOCF}_2\text{CF}_2\text{COOCH}_3$ with TFE	[32]		

Table 3: Chemical shifts and IR frequencies of [(α,β,β -trifluorovinyl)oxy] benzene functionalized by halogenosulfonyl or sulfonic acid groups.

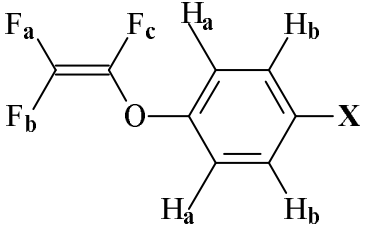
						
X	F_a	F_b	F_c	H_a	H_b	$\bar{\nu}$ (X)
δ (ppm)	δ (ppm)	δ (ppm)	δ (ppm)	δ (ppm)	δ (ppm)	(cm⁻¹)
Br (TFVOBB)	-119.8	-126.7	-134.9	7.1	7.5	-
SO₂Cl (TFVOBSC)	-117.8	-124.7	-136.1	7.2	8.1	1381 (O=S=O stretch)
SO₂F (TFVOBSF)	-117.1	-124.1	-136.2	7.4	8.2	1421 (O=S=O stretch)
SO₃H (TFVOBSA)	-115.1	-122.2	-137.1	7.5	8.1	3373 (S(O)(OH) ₂ stretch) 1029 (S(O)(OH) ₂ stretch)

Table 4: Determination of the Monomer/Terpolymer composition of VDF/Terolefin/ TFVOBB *versus* the reaction conditions in the radical terpolymerization of VDF, Terolefin (HFP or PMVE) with TFVOBB. Terpolymerization conditions : [2,5-Bis(*tert*-butylperoxy)-2,5-dimethylhexane]₀/([VDF]₀ + [Terolefin]₀ + [TFVOBB]₀) = 0.9 mol %, 134°C, 10 hours⁴⁷.

Exp. #	VDF in feed (mol %)	Terolefin in feed (mol %)	TFVOBB in feed (mol %)	VDF in terpolymer (mol %)	Terolefin in terpolymer (mol %)	TFVOBB in terpolymer (mol %)	Massic yields (%)
1	83	12 HFP	5	84	10 HFP	6	38
2	79	13 HFP	8	82	8 HFP	10	20
3	80	9 HFP	11	81	5 HFP	14	17
4	70	25 PMVE	5	78	15 PMVE	7	41
5	66	24 PMVE	10	72	13 PMVE	15	17
6	64	22 PMVE	14	71	10 PMVE	19	15

Table 5: ^{19}F -NMR assignments of fluorinated groups in the poly(VDF-co-HFP-co-TFVOBSC) terpolymers recorded in deuterated acetone.

Chemical shift (ppm)	structure	Integrals in (Eq. 1)
-70.9	$-\text{CH}_2\text{CF}_2\text{CF}_2\text{CF}(\text{CF}_3)-\text{CF}_2-\text{CH}_2-$	$I_{-70.9}$
-74.9	$-\text{CH}_2-\text{CF}_2-\text{CF}_2-\text{CF}(\text{CF}_3)-\text{CH}_2-\text{CF}_2-$	$I_{-74.9}$
-91.3	$-\text{CF}_2-\text{CH}_2-\text{CF}_2-\text{CH}_2-\text{CF}_2-$	$I_{-91.3}$
-95.1	$(\text{CH}_2-\text{CF}_2)-(\text{CF}_2-\text{CH}_2)-(\text{CH}_2-\text{CF}_2)-(\text{CH}_2-\text{CF}_2)$	$I_{-95.1}$
-109.7	$-\text{CH}_2\text{CF}_2\text{CF}_2\text{CF}(\text{CF}_3)-$	$I_{-109.7}$
-110.2	$-(\text{CH}_2-\text{CF}_2)-[\text{CF}_2-\text{CF}(\text{O}-\text{Ph}-\text{SO}_2\text{Cl})]-$	$I_{-110.2}$
-113.7	$-(\text{CH}_2-\text{CF}_2)-(\text{CF}_2-\text{CH}_2)-(\text{CF}_2-\text{CH}_2)-$	$I_{-113.7}$
-113.8	$-(\text{CH}_2-\text{CF}_2)-[\text{CF}_2-\text{CF}(\text{O}-\text{Ph}-\text{SO}_2\text{Cl})]-$	$I_{-113.8}$
-115.6	$-(\text{CH}_2-\text{CF}_2)-(\text{CF}_2-\text{CH}_2)-(\text{CH}_2-\text{CF}_2)-$	$I_{-115.6}$
-118.7	$-\text{CH}_2\text{CF}_2\text{CF}_2\text{CF}(\text{CF}_3)-$	$I_{-118.7}$
-124.5	$-(\text{CH}_2-\text{CF}_2)-[\text{CF}_2-\text{CF}(\text{O}-\text{Ph}-\text{SO}_2\text{Cl})]-$	$I_{-124.7}$
-184.1	$-\text{CH}_2\text{CF}_2\text{CF}_2\text{CF}(\text{CF}_3)-$	$I_{-184.1}$

Table 6: Determination of the Monomer/Terpolymer composition of VDF / Terolefin / TFVOBSC *versus* the reaction conditions in the radical terpolymerization of VDF, Terolefin (HFP or PMVE) with TFVOBSC. Terpolymerization conditions : [2,5-Bis(*tert*-butylperoxy)-2,5-dimethylhexane]₀/([VDF]₀ + [Terolefin]₀ + [TFVOBSC]₀) = 0.9 mol %, 134°C, 10 hours. Average molecular weights, M_n and M_w assessed from SEC with poly(styrene) standards. T_g were measured by DSC.

Exp. #	VDF mol % in feed	HFP or PMVE mol % in feed	TFVOBSC mol % in feed	VDF mol % in terpolymer	HFP or PMVE mol % in terpolymer	TFVOBSC mol % in terpolymer	Massic yields (%)	T _g (°C)	M _n (M _w) (g/mol)	PDI
7	87.6	9.5 HFP	2.9	90.5	5.9 HFP	3.6	17	-27	14200 (21300)	1.5
8	84.9	10.3 HFP	4.8	85.6	7.7 HFP	6.7	12	-21	10900 (17500)	1.6
9	81.7	10.5 HFP	7.8	94.5	5.5 HFP	0	2	-30	6200 (11800)	1.9
10	72.7	22.7 PMVE	4.6	74.1	17.1 PMVE	8.8	20	-31	16400 (24500)	1.5
11	79.4	10.4 PMVE	10.2	95.5	4.5 PMVE	0	4	-35	5800 (10800)	1.9

T_g stands for glass transition temperature

Table 7: ^{19}F -NMR assignments of fluorinated groups in the poly(VDF-co-PMVE-co-TFVOBSC) terpolymers recorded in deuterated acetone.

Chemical shift (ppm)	structure	Integrals in (Eq. 2)
-52.1	$-\text{CH}_2-\text{CF}_2-\text{CF}_2-\text{CF}(\text{OCF}_3)-\text{CH}_2-\text{CF}_2-$	$I_{-52.1}$
-91.1	$-\text{CF}_2-\text{CH}_2-\text{CF}_2-\text{CH}_2-\text{CF}_2-$	$I_{-91.1}$
-94.3	$-\text{CH}_2-\text{CF}_2-\text{CH}_2-\text{CF}_2-\text{CF}_2-\text{CH}_2-$	$I_{-94.3}$
-110.1	$-\text{CH}_2-\text{CF}_2-\text{CF}_2-\text{CF}(\text{OCF}_3)-\text{CH}_2-\text{CF}_2-$	$I_{-110.1}$
-110.8	$-(\text{CH}_2-\text{CF}_2)-[\text{CF}_2-\text{CF}(\text{O-Ph-SO}_2\text{Cl})]-$	$I_{-110.8}$
-113.1	$-\text{CH}_2-\text{CF}_2-\text{CH}_2-\text{CF}_2-\text{CF}_2-\text{CH}_2-$	$I_{-113.1}$
-113.4	$-(\text{CH}_2-\text{CF}_2)-[\text{CF}_2-\text{CF}(\text{O-Ph-SO}_2\text{Cl})]-$	$I_{-113.4}$
-115.8	$-\text{CH}_2-\text{CF}_2-\text{CF}_2-\text{CH}_2-\text{CH}_2-\text{CF}_2-$	$I_{-115.8}$
-120.8	$-\text{CF}_2-\text{CF}(\text{OCF}_3)-\text{CH}_2-\text{CF}_2-\text{CF}_2-\text{CF}(\text{OCF}_3)-\text{CH}_2-\text{CF}_2-$	$I_{-120.8}$
-122.2	$-\text{CH}_2-\text{CF}_2-\text{CF}_2-\text{CF}(\text{OCF}_3)-\text{CH}_2-\text{CF}_2-$	$I_{-122.2}$
-125.2	$-(\text{CH}_2-\text{CF}_2)-[\text{CF}_2-\text{CF}(\text{O-Ph-SO}_2\text{Cl})]-$	$I_{-125.2}$
-125.4	$-\text{CH}_2-\text{CF}_2-\text{CF}_2-\text{CF}(\text{OCF}_3)-\text{CH}_2-\text{CF}_2-$	$I_{-125.4}$
-145.3	$-\text{CH}_2-\text{CF}_2-\text{CF}_2-\text{CF}(\text{OCF}_3)-\text{CH}_2-\text{CF}_2-$	$I_{-145.3}$

Table 8: membrane characteristics prepared from ionomers A, B, and C

Membranes based on Ionomer	VDF mol % in ionomer	HFP or PMVE mol % in ionomer	TFVOBSA mol % in ionomer	IEC (mEq H ⁺ / g)	Proton conductivity σ (mS / cm)	Swelling rates (%)	T _g (°C)	T _d (°C) at 10 % under air
A	90.5	5.9 HFP	3.6	0.4	0.037	44	-21	238
B	85.6	7.7 HFP	6.7	0.5	0.059	57	-14	231
C	74.1	17.1 PMVE	8.8	0.6	0.082	88	-25	225

T_g stands for glass transition temperature
T_d stands for decomposition temperature

FIGURE CAPTIONS:

Figure 1: ^1H NMR spectrum of poly(VDF-*ter*-HFP-*ter*-TFVOBSC) terpolymer, recorded in deuterated acetone. Terpolymerization conditions: [2,5-Bis(*tert*-butylperoxy)-2,5-dimethylhexane]₀/([VDF]₀ + [HFP]₀ + [TFVOBSC]₀) = 0.9 %, 134°C, 6 hours and VDF / HFP / TFVOBB initial molar ratio in the feed = 84.9/10.3/4.8.

Figure 2: ^{19}F NMR spectrum of poly(VDF-*ter*-HFP-*ter*-TFVOBSC) terpolymer, recorded in deuterated acetone. Terpolymerization conditions: [2,5-Bis(*tert*-butylperoxy)-2,5-dimethylhexane]₀/([VDF]₀ + [HFP]₀ + [TFVOBSC]₀) = 0.9 %, 134°C, 6 hours and VDF / HFP / TFVOBSC initial molar ratio in the feed = 87.6 / 9.5 / 2.9 (exp #7 Table 6)

Figure 3: ^{19}F NMR spectrum of poly(VDF-*ter*-PMVE-*ter*-TFVOBSC) terpolymer, recorded in deuterated acetone. Terpolymerization conditions: [2,5-Bis(*tert*-butylperoxy)-2,5-dimethylhexane]₀/([VDF]₀ + [PMVE]₀ + [TFVOBSC]₀) = 0.9 %, 134°C, 6 hours and VDF / PMVE / TFVOBSC initial molar ratio in the feed = 72.7 / 22.7 / 4.6 (exp #10 Table 6).

Figure 4: TGA thermogram of poly(VDF-*ter*-HFP-*ter*-TFVOBSC) terpolymers: % mol monomers in the terpolymer 90.5 / 5.9 / 3.6 : VDF / HFP / TFVOBSC : \triangle ; % mol monomers in the terpolymer 85.6 / 7.7 / 6.7 : VDF / HFP / TFVOBSC : \square)

Figure 1: ^1H NMR spectrum of poly(VDF-*ter*-HFP-*ter*-TFVOBSC) terpolymer, recorded in deuterated acetone. Terpolymerization conditions: [2,5-Bis(*tert*-butylperoxy)-2,5-dimethylhexane]/([VDF]₀ + [HFP]₀ + [TFVOBSC]₀) = 0.9 %, 134°C, 6 hours and VDF / HFP / TFVOBB initial molar ratio in the feed = 84.9/10.3/4.8.

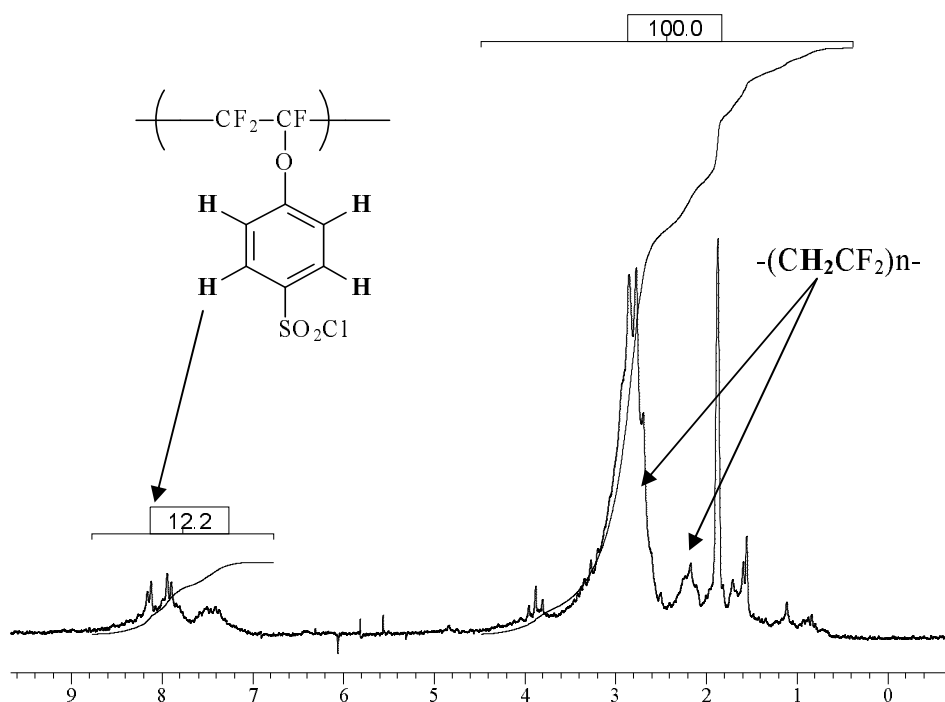


Figure 2: ^{19}F NMR spectrum of poly(VDF-*ter*-HFP-*ter*-TFVOBSC) terpolymer, recorded in deuterated acetone. Terpolymerization conditions: $[2,5\text{-Bis(}i\text{tert-butylperoxy)-2,5-dimethylhexane}]_0 / ([\text{VDF}]_0 + [\text{HFP}]_0 + [\text{TFVOBSC}]_0) = 0.9\%$, 134°C , 6 hours and VDF / HFP / TFVOBSC initial molar ratio in the feed = 87.6 / 9.5 / 2.9 (exp #7 Table 6).

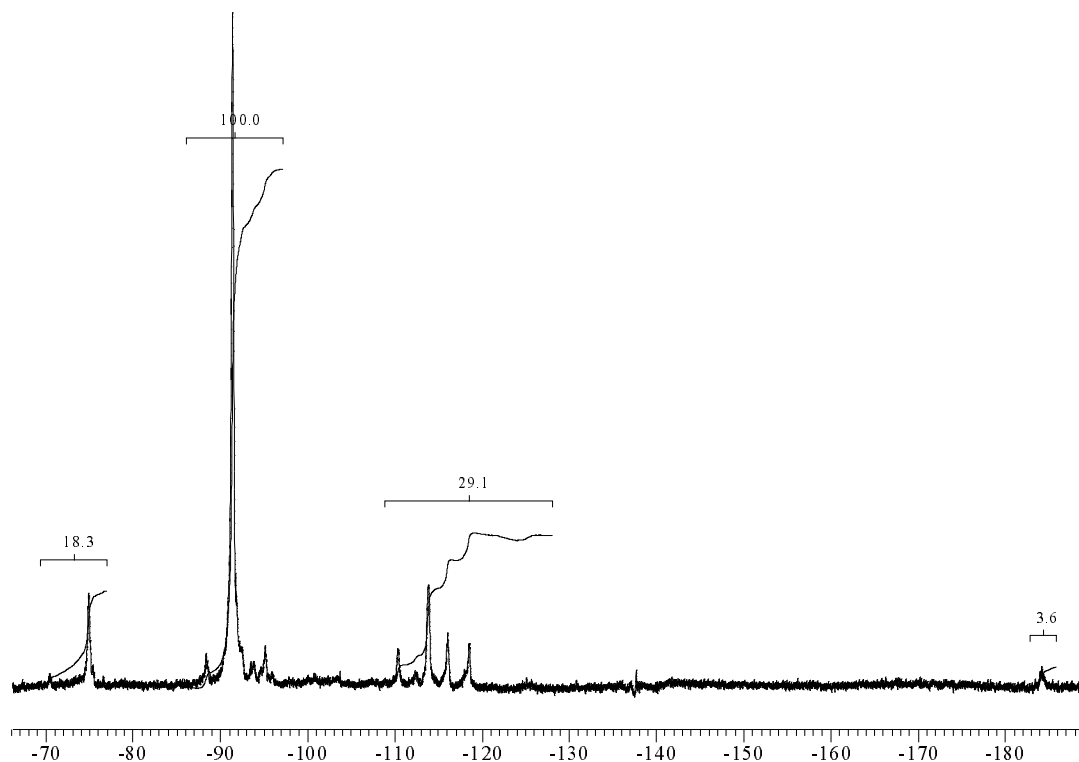


Figure 3: ^{19}F NMR spectrum of poly(VDF-*ter*-PMVE-*ter*-TFVOBSC) terpolymer, recorded in deuterated acetone. Terpolymerization conditions: $[2,5\text{-Bis(}i\text{tert-butylperoxy)-2,5-dimethylhexane}]_0 / ([\text{VDF}]_0 + [\text{PMVE}]_0 + [\text{TFVOBSC}]_0) = 0.9\%$, 134°C , 6 hours and VDF / PMVE / TFVOBSC initial molar ratio in the feed = 72.7 / 22.7 / 4.6 (exp #10 Table 6).

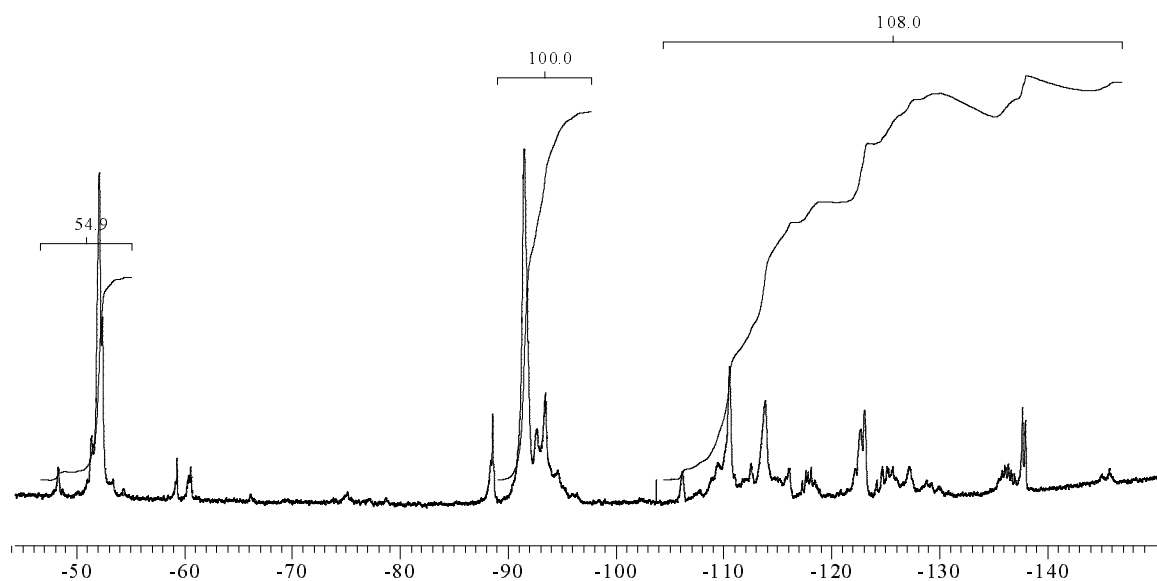


Figure 4: TGA thermogram of poly(VDF-*ter*-HFP-*ter*-TFVOBSC) terpolymers: % mol monomers in the terpolymer 90.5 / 5.9 / 3.6 : VDF / HFP / TFVOBSC : \triangle ; % mol monomers in the terpolymer 85.6 / 7.7 / 6.7 : VDF / HFP / TFVOBSC : \square)

